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High Resolution Chemistry Based Modeling of LLM-105 Explosives

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Abstract. LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide) is an insensitive high explosive which has performance between that of HMX and TATB. It is insensitive to shock, spark and friction and has an impact insensitivity level approaching that of TATB. These properties make it a realistic high-performance insensitive high explosive material, attractive for applications that require moderate performance and insensitivity. Several LLM-105 morphologies and plastic-bonded formulations have been prepared and their detonation performance has been experimentally studied. We present chemistry based modeling of these formulations and experiments using the thermochemical code CHEETAH linked to a multi-dimensional ALE hydrodynamics model. Using CHEETAH we explicitly specify the explosive material composition and initial density. We show that CHEETAH is able to accurately model the different LLM-105 based explosives formulations over a wide range of densities using the same single burn rate model.

Introduction

LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide) is newly developed insensitive high explosive (IHE). It has excellent thermal stability, few cold-performance effects and performance between that of HMX and TATB[1]. Its calculated energy content is about 85% that of HMX and 15% more than that of TATB. It is insensitive to shock, spark and friction and has an impact insensitivity level approaching that of TATB. These combined properties make it a realistic high-performance IHE material, attractive for applications that require moderate performance and insensitivity.

Several LLM-105 morphologies and plastic-bonded formulations have been prepared over a range of densities, and their detonation performance has been experimentally studied. The rate of development for new LLM-105 formulations has been limited by the synthesis and manufacturing considerations. The original synthesis route used dimethoxy pyrazine (DMP) as a starting reagent. This route has been refined to increase yields, and reduce impurities and costs. The DMP route produces high quality crystals having of modest (40-50 um) mean size. However, this route also yields 5-10% ANPZ (2,6-diamino-3,5-dinitropyrazine) - a co-product having lower density (1.800 g/cc) and less energy than LLM-105. A second route was developed recently that uses significantly less expensive starting reagents to produce a stable intermediate, DAPO (2,6-diamino-pyrazine-1-oxide).[2] This intermediate is a non-explosive that can be manufactured in quantity and nitrated in a single step in a separate, controlled process. This results in a safer, and less costly manufacturing path. The new synthesis yields a very pure product with good yield. However, the new route yields a smaller (~20um) crystal, resulting in more challenging formulation and parts fabrication issues.

The changing synthesis and manufacturing paths have led to a variety of research formulations

being developed at Livermore. Most all of the formulations have been PBX's - plastic bonded explosives. PBX's are first formulated into molding powders, and then compacted under high loads (20-30 kpsi) to shape, or into a part that can machined to the desired shape. The performance is heavily dependent upon the power density and quality of compaction. And the compaction process is highly dependent on the size and shape of the explosive crystals. The LLNL research formulations have attempted to balance energy content with good compaction qualities, by varying the type and amount of binder. Viton-A (DuPont), KELF-800 (old Kel-F), and FK-800 (new Kel-F from 3M) are the binders used in this study. Increased binder content can generally help improve compaction, but results in a part having lower density and energy content. A second method for achieving better compaction is to use a combination of coarse and fine explosive crystals. The fine crystals are made from a milling process (either fluid energy milling or ball milling), and are combined with the coarse particles in a 1:3 ratio. This bimodal distribution of particle size usually results in a compacted part having 1-2% higher density than the mono-modal formulation. Table 1 shows the composition, synthesis route and particle description used for each formulation discussed in this paper.

We present here a chemistry based modeling of wall and foil experiments for LLM-105 base explosives using the thermochemical code CHEETAH3[3-4] linked to a multi-dimensional ALE hydrodynamics model.
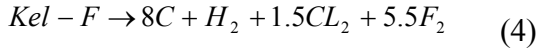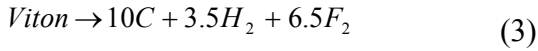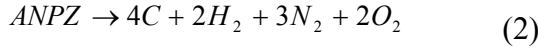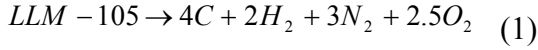
Model

CHEETAH is a multi-phase first principle based equation of state model which uses as its starting point exponential 6 molecular dynamics modeling. The linked CHEETAH-ALE model treats slowly reacting chemical species using kinetic rate laws, with chemical equilibrium assumed for species coupled via fast time-scale reactions. Typically greater than 30 species and phases are simultaneously treated. This results in a flexible, self-consistent treatment of the equation of state which allows for significant variations in concentrations of condensed and gaseous species with time.

The CHEETAH model we have developed can accurately treat different LLM-105 based explosives by simply specifying their chemical composition and the initial explosive density. Differing binder materials (Viton and Kel-F), and binder concentrations are considered. The differences between various binder formulations for Viton and Kel-F were ignored modeling as the binder concentration was only a few per cent of the total explosive.

Table 1: Formulation Matrix for LLM-105-based PBX's

Formulation	Binder	Wt. Pct. Binder	Synthesis	Crystal Mix
RX-55-AB	KelF-800	7.6	DMP	monomodal
RX-55-AY	Viton-A	6	DMP	bimodal
RX-55-BI	Viton-A	6	DMP	bimodal
RX-55-BJ	Viton-A	6	DAPO	monomodal
RX-55-BK	Viton-A	6	DMP	bimodal
RX-55-BP	FK-800	5	DAPO	monomodal
RX-55-BS	FK-800	5	DAPO	monomodal
RX-55-BT	Viton-A	6	DMP	bimodal

We include separate kinetic rate equations for the transformation of LLM-105, binder, and possible contaminates into products. Use of the same rate for each of these materials was found to be adequate to allow them to be simultaneously burned to products species. The growth of a small particulate form of condensed graphite to a large particulate form is also considered. The kinetic reactions treated were:

$$LLM-105 \rightarrow 4C + 2H_2 + 3N_2 + 2.5O_2 \quad (1)$$

$$ANPZ \rightarrow 4C + 2H_2 + 3N_2 + 2O_2 \quad (2)$$

$$Viton \rightarrow 10C + 3.5H_2 + 6.5F_2 \quad (3)$$

$$Kel-F \rightarrow 8C + H_2 + 1.5CL_2 + 5.5F_2 \quad (4)$$

and

$$C_S \rightarrow C_B \quad (5)$$

Note that the chemical composition of LLM-105 and the contaminant ANPZ are very similar. This similarity resulted in our simulations showing a very small difference in energy release between pure LLM-105 and samples contaminated with ANPZ. In the above, C_S and C_B refer to small and large carbon graphite clusters which represent the effective initial and final graphite concentrations.

The kinetic burn rates used have the following form

$$\frac{dF}{dt} = A(1 - F_2 - \lambda)^B (P + Q)^C$$
$$\frac{dF}{dt} = 0 \ if \ \lambda \geq 1 - F_2$$
$$= 0 \ if \ P + Q < P_1 \ and \ \lambda < F_1 \quad . \quad (6)$$
$$= \frac{dF}{dt}\left(\frac{P + Q}{P_2}\right)^D \ if \ \lambda < F_3$$
$$= 0 \ if \ P + Q < P_3 \ and \ \lambda < F_3$$

F is the HE burn mass fraction. λ is ration of F to its initial value. Q is the artificial viscosity. A, B, C, D, F_1, F_2, F_3, P_1, P_2, and P_3 are constants. The effective pressure $P + Q$ (rather than P) was used in the local pressure power law terms to be consistent with the use of the effective pressure in the hydrodynamic modeling of the momentum and energy equations. Arrhenius kinetics are used for carbon cluster growth

$$\frac{dC_B}{dt} = A C_s e^{-T_C^*/T} \quad . \quad (7)$$

The rate controlled species are LLM-105, ANPZ, Viton, Kel-F, and C_B. Species concentrations that are not kinetic rate controlled are calculated as being in chemical equilibrium for pressures greater than a specified "freeze pressure" P_F, and are held approximately constant below this pressure.

Calibration

To calibrate the LLM-105 based explosive kinetic rates we used copper cylinder and Disc Acceleration eXperiment[5] (DAX) data. Figure 1 shows a schematic of the experimental setup. In the DAX experiment a thin (10-16 mil) foil was rapidly accelerated by the detonation wave as it reaches the end of weakly confined cylinder disks. The acceleration time scale to reach terminal velocity was few microseconds For the LLM-105 based explosives considered here the estimated detonation reaction zone was ~0.1mm, which was comparable to the foil thickness. The foil velocity was only sensitive to detonation wave pressures close to detonation wave front. The copper cylinder side wall acceleration on the other hand occurs over tens of microseconds. This longer acceleration time scale makes the cylinder wall velocity weakly dependent upon the reaction zone and only sensitive to the late time adiabatic regime of the detonation wave. The data from these two different experiments are thus complementary in being sensitive to different regions of the detonation wave.

To fully resolve the detonation reaction zone for our LLM-105 based explosives and the DAX foil required spatial mesh resolution on the order of 1000 zones/cm. Two dimensional, cylindrically symmetric simulations of the cylinder or DAX experiments using a uniform mesh with this
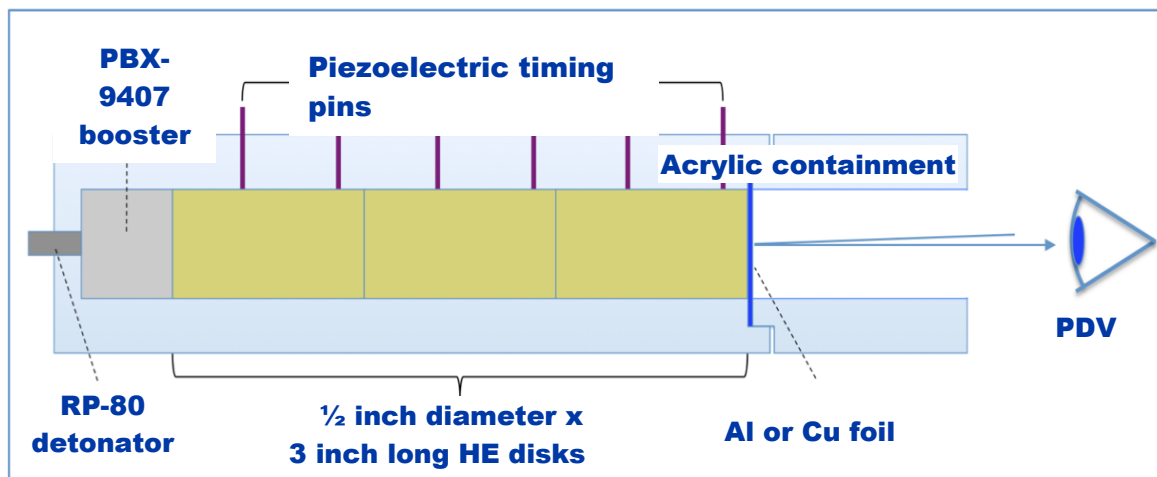
Fig. 1. DAX experimental geometry.

resolution would have required tens of millions of zones. Instead we used Automatic Mesh Refinement (AMR) to allow dynamic changes in the mesh spacing. We used four levels of mesh refinement from 30 to 810 zones/cm. Regions of highest spatial resolution were at the detonation wave front and in the foil. The copper cylinder experiments for wall velocity or breakout timing were less sensitive to how well the detonation wave reaction zone was resolved. A 320 zones/cm uniform mesh was found sufficient for our copper cylinder simulations. Comparisons between this uniform meshing and our higher resolution AMR mesh showed no significant differences.

Experimental Data

The eight different plastic bonded variants of LLM-105 shown in Table 1 were included in our calibration. Several different synthesis processes were used in manufacturing methods for LLM-105 result in varying amounts contaminants of which ANPZ dominated. ANPZ contamination was ~5% for DMP synthesis formulations. Mass fractions of LLM-105, Viton, Kel-F, and ANPZ were explicitly specified for each RX-55 variant in our CHEETAH model. Detailed comparisons of simulations assuming pure LLM-105 as compared to LLM-105 contaminated with ~5% ANPS were extremely similar in behavior.

One inch diameter copper cylinder detonation experiments were done at LLNL for RX-55-AB and RX-55-BS, with respective densities of 1.825 g/cc and 1.861 g/cc. DAX experiments were done for RX-55-AY, RX-55-BI, RX-55-BJ, RX-55-BK, RX-55-BP and RX-55-BT, with respective densities of 1.832 g/cc, 1.818 g/cc, 1.818 g/cc, 1.818 g/cc, 1.859 g/cc, and 1.833 g/cc. The HE densities for the DAX experiments correspond to the density of the last pellet before the foil. For RX-55-AY a 16-mil aluminum foil was used, while a 10-mil copper foil was used for all the other DAX experiments.

Model calibration

Our model rate calibration used the breakout timing data from the RX-55-AB one inch diameter copper cylinder. The shape of the breakout is sensitive to the value of the explosive burn rate which determines the detonation wave front curvature. Figure 2 shows a comparison between the simulation and experimental break out timing after our rate calibration. The curve labeled Rate * 0.8 corresponds to the simulation breakout timing if the burn rates were reduced by a factor of 0.8. This indicates that our rate fitting was sensitive to roughly 20% variations. Figure 3 shows the simulation pressure profile slightly before breakout showing how slight the detonation wave

curvature is. Detonation curvature for RX-55-AB, and presumably for all the LLM-105 based explosives considered here, is much smaller than that for LX-17 (92.5% TATB, 7.5% Kel-F), or PBX9502 (95% TATB, 5% Kel-F). To match the breakout timing we were required to use a burn rate roughly 20 times greater than that for LX-17 or PBX9502. This implies that the LLM-105 based explosives have a considerably smaller reaction zone than TATB based explosives. As LLM-105 was the dominant component for each explosive considered here we assumed that the burn rates were the same for all RX-55 variant. A sensitivity study showed that variations in the burn rate of up to a factor of 2 did not significantly modify our results.
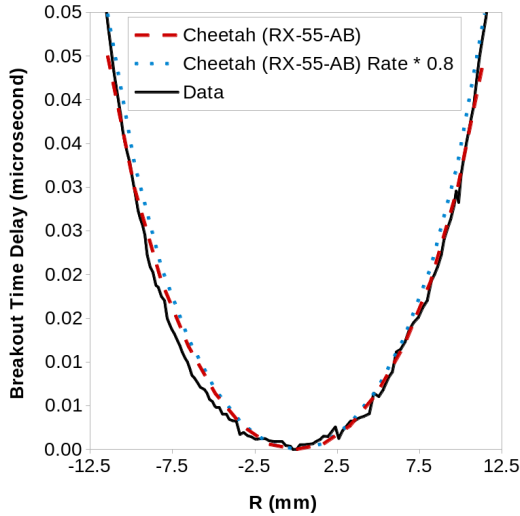
Fig. 2. Comparison between breakout timing from CHEETAH simulation and one inch RX-55-AB copper cylinder data. The solid curve gives the experimental breakout timing. The dashed curve shows results from our calibrated rate model, while the dotted curve represents simulation breakout timing done with the burn rate reduced by a factor of 0.8.
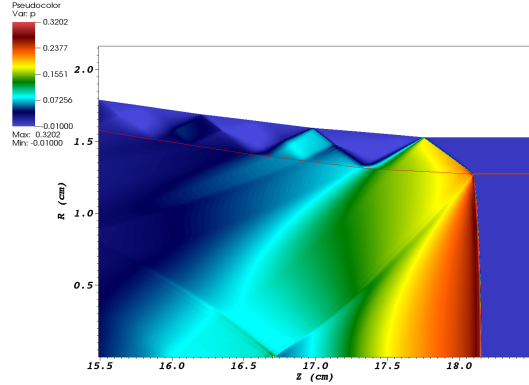

Fig. 3. Simulation copper cylinder pressure profile showing how slight the detonation wave curvature is for RX-55-AB.

The DAX experiment foil velocity is sensitive to the detonation wave reaction zone, and very weakly dependent on the detonation pressure behind the CJ point. This selective sensitivity was used in our model calibration to separate early time vs. late time energy release effects. Figures 4-5 show DAX simulation pressure profiles slightly before and after the copper foil is accelerated. Figure 5 shows a strong reflected shock traveling back from the foil and a strong drop in pressure behind the foil.
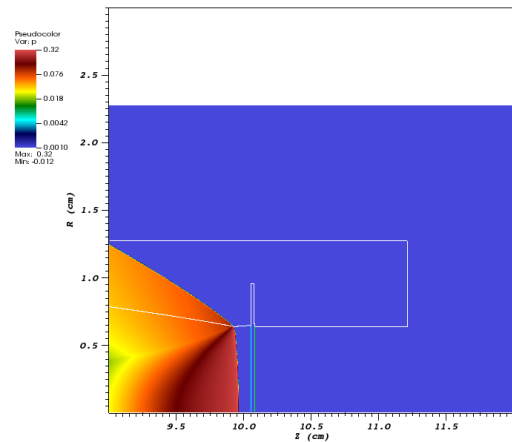

Fig. 4. Simulation copper foil DAX pressure profile slightly before the detonation wave reaches the foil.
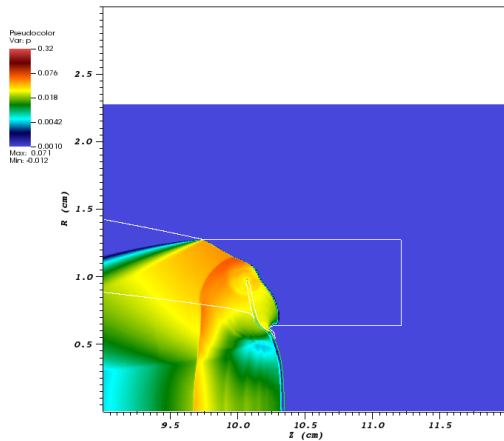
Fig. 5 Simulation copper foil DAX pressure profile slightly after the detonation wave reaches the foil.

The copper cylinder wall velocity is sensitive to the CHEETAH "freeze" pressure value, which is much smaller than the CJ pressure. This is a long time scale modification to the detonation wave which is applied well after the reaction zone. The "freeze" pressure value does not affect the detonation velocity or breakout timing, and has little effect on the DAX foil velocity. The copper cylinder wall velocity is strongly dependent upon the CJ pressure. Getting good agreement with both the copper cylinder wall velocity and the DAX foil velocity is a good indication of the accuracy of our modeling of both the reaction zone, the CJ pressure, and the late time pressure release wave.

Results

After calibration we were able to easily model the DAX LLX-105 experiments by simply specifying the initial mass fractions and initial density of each explosive. Figure 6-8 respectively compare our simulation results to data for RX-55-AY, RX-55-BP and RX-55-BT. This comparison considers different flyers, binders and densities. The RX-55-AY case used an aluminum foil and a Viton binder. The RX-55-BP and RX-55-BT cases used copper foils which accelerate more slowly than the aluminum foil. RX-55-BP uses a Viton binder, while RX-55-BT used Kel-F as the

binder. Good agreement is evident over a density range of 1.832-1.861 g/cc and for both binders. Early time aluminum and copper foil oscillations in the simulations was sensitive to the metal EOS model used and is likely the main source of disagreement with experimental data.
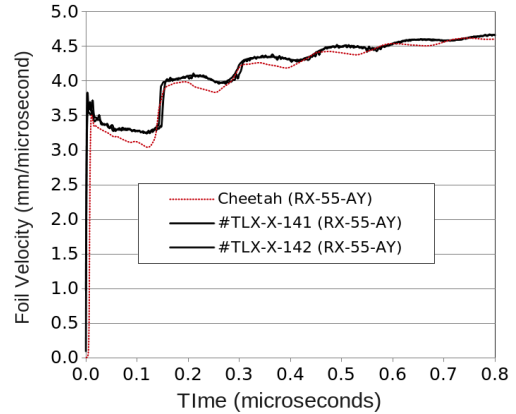

Fig 6 DAX aluminum foil velocity on axis for RX-55-AY at 1.832 g/cc with a Viton binder.
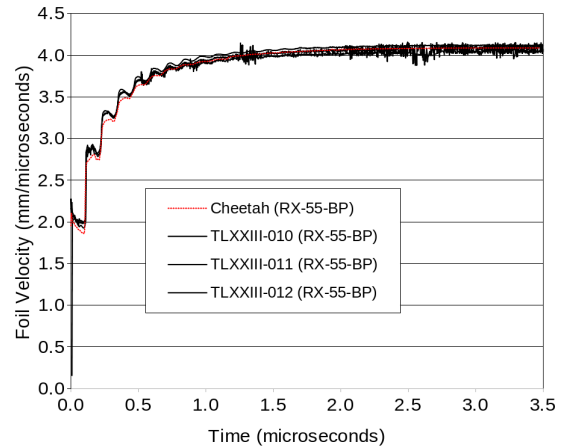

Fig 7. DAX copper foil velocity on axis for RX-55-BP at 1.832 g/cc with a Kel-F binder. Note that the initial jump-off velocity and the acceleration are lower for the copper foil than for the aluminum foil.
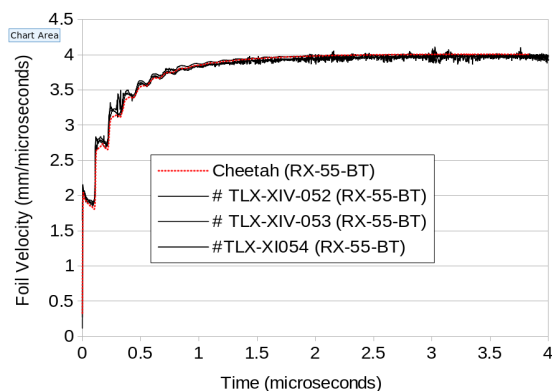
Fig 8. DAX copper foil velocity on axis for RX-55-BT at 1.833 g/cc with a Viton binder.

Next we show how well our model matches the lower velocity and longer time scale copper cylinder data. Figure 9 compares RX-55-BS experimental and simulation data. The wall acceleration is much reduced, and lasts for tens of microseconds instead of just a few microseconds as is the case for the DAX experiment.
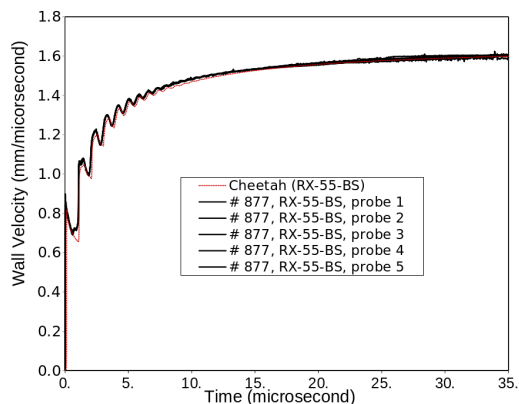

Fig 9. Copper cylinder wall velocity for RX-55-BS at 1.861 g/cc with a Kel-F binder.

Conclusions

We have shown here how a chemistry based model for LLM-105 base explosives can be used to treat the different formulations, binders, densities, and time scales. Our model agrees well with breakout timing, short time scale DAX foil acceleration, and long time scale copper cylinder wall acceleration. Out model can be used to predict sensitivity to density, contaminants, and binders for new LLM-105 based explosive formulations.

Auspices Statement

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